A-13

Excited State Axial Ligation in Metalloporphyrins as Revealed by Transient X-ray Absorption Spectroscopy

Lin X. Chen[1, 2], Xiaoyi Zhang[3], Erik C. Wasinger[1], Jenny V. Lockard[1], Andrew B. Stickrath[1], Michael W. Mara[2], Klaus Attenkofer[3], Guy Jennings[3], Grigory Smolentsev[4], and Alexander Soldatov[4]

[1]Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439
[2]Department of Chemistry, Northwestern University, Evanston, IL 60208
[3]X-ray Sciences Division, Argonne National Laboratory, Argonne, IL 60439
[4]Physics Department, Southern Federal University, Rostov-na-Donu 344090 Russia

The photoinduced axial ligation mechanism of a metalloporphyrin, nickel(II) tetramesitylporphyrin (NiTMP) is investigated by transient x-ray absorption spectroscopy at the Ni K-edge (8.333 keV). Photoexcitation of the porphyrin Q-band induces a ($3d_{z2}$, $3d_{x2-y2}$) configuration and promotes axial ligation. The x-ray transient absorption at 1s → $4p_z$ transition energy taken at different time delays after the photoexcitation presents a time sequence of the excited state and ligation processes. A unified axial ligation reaction mechanism for the ground state and the photoexcited state is proposed based on the elucidation of the excited state structural dynamics by transient optical and x-ray absorption spectroscopy as well as by density functional theory calculations. The results obtained from this study can be broadly applied to study other metalloporphyrins and metal complexes for their photocatalytic activities involving the transient ligation.

We would like to acknowledge the supports by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contracts DE-AC02-06CH11357. Work at the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.